

PRODUCTION OF $\text{SiO}_2\text{--P}_2\text{O}_5\text{--CaO--(Na}_2\text{O)}$ STRUCTURED FILMS

T. S. Petrovskaya^{1,3} and L. P. Borilo¹

Translated from *Steklo i Keramika*, No. 1, pp. 25 – 29, January, 2012.

The sol-gel method is used to obtain from film-forming solutions, based on solutions of tetra-ethyl-ortho-silicate and phosphoric acid with addition of calcium and sodium salts, thin structured films in the systems $\text{SiO}_2\text{--P}_2\text{O}_5\text{--CaO--(Na}_2\text{O)}$ with the following content by weight (wt.%): 10 – 85 SiO_2 , 5 – 40 P_2O_5 , 10 – 50 CaO, and 10 Na_2O . The physical-chemical processes in solutions giving rise to a transition of the true solutions into colloidal solutions via successive sol and gel states are studied. A criterion is established for the film-forming power: the viscosity of the solutions. The critical value of the viscosity for obtaining high-quality films is determined. Oxide systems form in films during kilning to temperature 600°C. The structure of the films is investigated by means of infrared spectroscopy, atomic-force microscopy, and x-ray phase analysis. The surface of the films is characterized by an extended relief and porosity, so that it should have high adhesion properties. The thickness of the films obtained does not exceed 90 nm.

Key words: sol-gel method, film-forming solution, silicophosphate materials.

The problem of developing new materials with prescribed properties is one of a number of key problems of modern materials science and, in particular, medical materials science. For a number of reasons, sol-gel (SG) methods have obvious prospects for solving this problem [1]. In the sol-gel process the components interact at the molecular level and a high degree of product homogeneity obtains in multicomponent systems. Sol-gel methods make it possible to control the transition from an amorphous into a crystalline state without introducing mineralizing additives as well as to obtain monolithic articles, highly disperse powders, and thin films on different substrates [2]. Sol-gel technologies make it possible to obtain high-purity materials at low temperatures by introducing micro quantities of substances, which is of great value for obtaining biomaterials [2, 3].

The principles of producing nanostructured films and dispersions as well as the physical-chemical processes in a double silicophosphate system are examined in [3, 4].

The objective of the present work is to investigate the possibility of obtaining by the SG method structured films in the system $\text{SiO}_2\text{--P}_2\text{O}_5\text{--CaO--(Na}_2\text{O)}$ and to study their structure.

The procedure described in [3, 4] was used to prepare the solutions for synthesizing the films (film-forming solutions — FFS) for oxide systems in the composition range (%⁴)

10 – 85 SiO_2 , 5 – 40 P_2O_5 , 10 – 50 CaO, and 10 Na_2O . The initial materials consisted of tetra-ethyl-ortho-silicate (TEOS), orthophosphoric acid, calcium chloride, and sodium chloride. The films were formed on silicon substrates by centrifuging (centrifuge rotation rate 3000 rpm) and drawing (draw velocity to 30 cm/min). The films were secured by heat-treatment in two stages: at 60°C (1 h) and 600 – 800°C (30 min). The viscosity of the solutions was measured with a glass viscosimeter (VPZh-2, capillary diameter 0.99 mm). The infrared spectra of the films were recorded in the frequency range 400 – 4000 cm^{-1} using a Perkin Elmer FTIR-Spectrometer. The phase composition of the disperse products was determined with a DRON-3M diffractometer and atomic-force microscopy was performed on the NtegraAURA station. The thickness and index of refraction of the films obtained were investigated with an LÉF-3M laser ellipsometer ($\lambda = 632.8 \text{ nm}$); the measurements were performed at five points along the entire surface of the films for each sample, and the optical parameters were calculated using a model of a uniform, nonabsorbing layer on an isotropic substrate.

To formation of films from solutions is based on the capability of the initial substances to enter into a hydrolytic polycondensation reaction and to form colloidal solutions [1, 3], in the course of whose aging the mass of the particles increases with the viscosity changing in consequence. Figures 1 – 3 display plots of the viscosity of FFS of the corresponding three- and four-component oxide systems versus the aging time. As can be seen from the figures, the viscosity of the solutions increases during the first few days and de-

¹ Tomsk Polytechnical University, Tomsk, Russia.

² Tomsk State University, Tomsk, Russia.

³ E-mail: pts@tpu.ru.

⁴ Here and below, content by weight, unless stipulated otherwise.

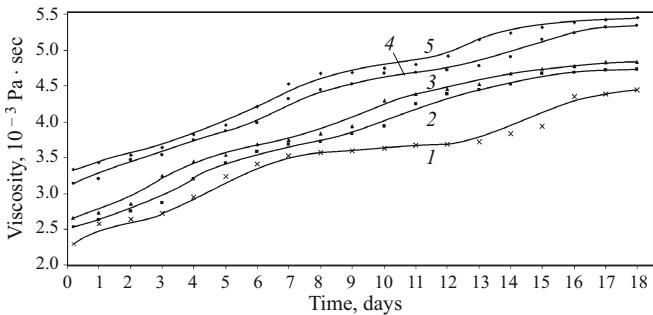


Fig. 1. Viscosity of film-forming solutions versus the aging time for the three-component system $\text{SiO}_2\text{-P}_2\text{O}_5\text{-CaO}$ with 20 wt.% P_2O_5 and CaO content increasing from 10 to 50 wt.% in the series of solutions 1 – 5.

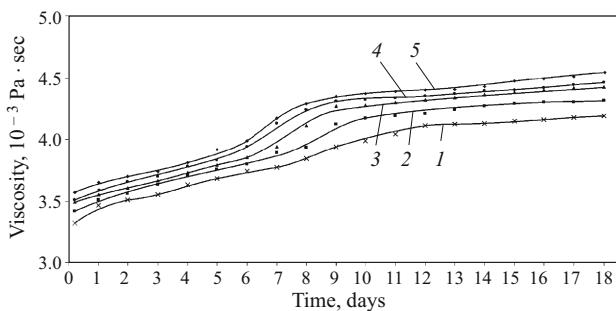


Fig. 2. Viscosity of film-forming solutions versus the aging time for the four-component system $\text{SiO}_2\text{-P}_2\text{O}_5\text{-CaO-Na}_2\text{O}$ with 10 wt.% Na_2O , 20 wt.% P_2O_5 and CaO content increasing from 10 to 50 wt.% in the series of solutions 1 – 5.

pends on the chemical composition of the solution. In [3, 4] it was found that the viscosity η_{day} of a solution after aging for 1 day for TEOS is 1.9×10^{-3} Pa · sec, while the viscosity of solutions for obtaining two-component oxide systems is in the range $(2.3 - 2.7) \times 10^{-3}$ Pa · sec, increasing with the content of phosphoric acid, which in terms of P_2O_5 corresponds to a change of the latter from 10 to 30%. To obtain three-component oxide systems with increasing calcium chloride concentration in solution, corresponding to a change of the calcium chloride concentration from 10 to 50%, the value of η_{day} of FFS varies in the range $(2.6 - 3.5) \times 10^{-3}$ Pa · sec in the series with 20% P_2O_5 (Fig. 1), $(3.6 - 4.1) \times 10^{-3}$ Pa · sec with 30% P_2O_5 , and $(4.1 - 4.7) \times 10^{-3}$ Pa · sec with 40% P_2O_5 .

For four-component compositions with 10% Na_2O and CaO content increasing from 10 to 50% the value of η_{day} in the initial FFS is in the range $(3.4 - 3.6) \times 10^{-3}$ Pa · sec with 15% P_2O_5 (Fig. 2), $(3.5 - 3.7) \times 10^{-3}$ Pa · sec with 25% P_2O_5 , and $(3.6 - 3.7) \times 10^{-3}$ Pa · sec for 35% P_2O_5 .

Thus, it is evident already at the initial stage of aging of the solutions that as the phosphoric acid concentration increases, hydrolysis and polycondensation processes are activated. As a result, the viscosity increases more rapidly in so-

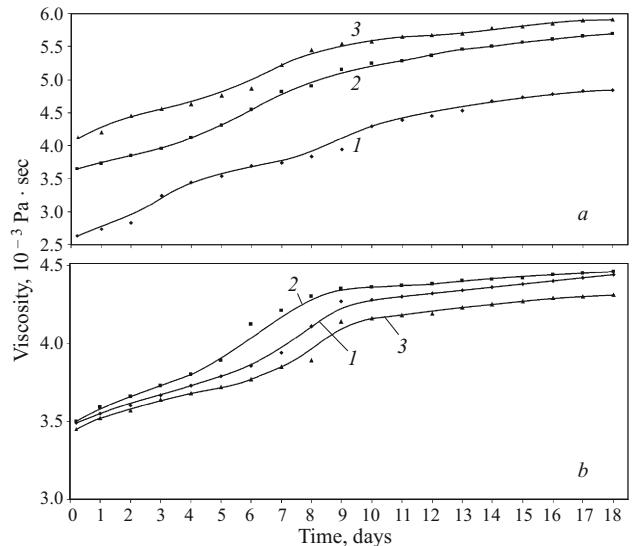
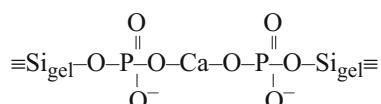


Fig. 3. Viscosity of film-forming solution versus the storage time for three- (a) and four-component (b) systems with 30 wt.% CaO and P_2O_5 increasing in the series of solutions 1 – 3 from 20 to 40% (three-component system) and in the series 1 – 3 from 15 to 35% (four-component system).

lutions for obtaining three-component oxide systems compared with solutions for obtaining two-component systems and in solutions for obtaining four-component systems compared with solutions for obtaining three-component systems (Fig. 3).

The tendency for the viscosity to increase is supported by further development of hydrolytic polycondensation processes during the last period of solution aging. The initial pH of the solutions from TEOS to the maximum phosphoric acid content varies in the interval 2 – 3.5. Increasing the acidity of the medium at the initial stage with introduction and subsequent increase of the phosphoric acid concentration in solutions for synthesis of two- and polycomponent oxide systems accelerates hydrolysis and polycondensation processes and, in consequence, increases the FFS viscosity (see Fig. 3). As one can see in the figure, introducing and increasing the concentration in the initial solution of calcium and sodium salts also increases the viscosity. One obvious reason is an increase of the content of hydroxyl groups as a result of the interaction of calcium and sodium chlorides with water, which promotes the development of hydrolytic polycondensation processes. Apparently, another reason is the interaction of silanol groups with the phosphate component in a neutralization reaction, which, in the opinion of the authors of [5], occurs in such solutions, and then interaction of the reaction product with calcium ions, which stabilizes the silicate gel owing to the formation of the three-dimensional structure



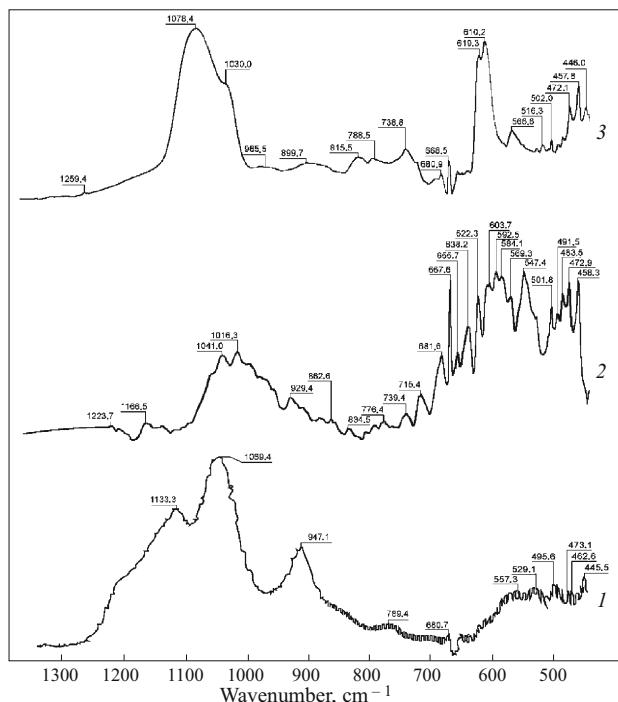


Fig. 4. IR spectra of films corresponding to the composition No. 43: 1) after deposition at 25°C; 2) after kilning at 500°C; 3) after kilning 800°C.

The presence of the double salt Ca₅(PO₄)₂SiO₄, which decomposes on heating in the temperature range 400–440°C, in the products of crystallization of the xerogel dispersions studied in the present work (according to XPS data) is a point in favor of such an interaction.

The character of the time dependence of the viscosity makes it possible to single out conventionally three stages of the processes occurring in solution. The first stage develops from the moment the solution is prepared and continues up to two days of aging depending on the compositions. It is due to a transition of the true solution into a colloidal solution as a result of hydrolysis and polycondensation processes resulting in the formation of a sol and is characterized by comparatively rapid growth of the viscosity.

The second stage is limited by the period after the second day, which determines the attainment of the maximum viscosity at which a film is formed. This value of the viscosity, equal to about 5×10^{-3} Pa · sec, was established experimentally for the experimental solutions and probably is due to some stabilization of the solution in the sol state — free-disperse system. Solutions with viscosity to 5×10^{-3} Pa · sec possess fluidity adequate for wetting a surface uniformly and forming a layer with uniform thickness.

The duration of the second stage is determined by the ratio of TEOS and orthophosphoric acid in solution, decreasing with increasing acid content. Thus, in the FFS of the corresponding three-component oxide systems, as the CaO content increases from 10 to 50% the duration of the second

TABLE 1. Characteristics of IR Spectra of Films with Composition No. 43

Presence of bands in the IR spectra, cm ⁻¹ , at kilning temperature, °C					Vibrations (type)
25	60	150	500	800	
3393.8	3458.6	3389.2	—	—	Adsorbed water (OH stretching vibrations)
	3376.4				
2918.8	2918.7	2920.1	—	—	C–H stretching vibrations
2850.3	2849.7	2847.5			
1631.0	1634.0	1633.8	—	—	Water deformation vibrations
1469.4	1467.9	1427.3	—	—	CH ₂ , CH ₃ deformation vibrations
—	—	—	1166.5	1259.4	OH deformation vibrations
1069.0	1069.4	1070.0	1040.1	1078.0	P=O, PO ₃ ²⁻ -group stretching vibrations
950.4	947.1	947.8	929.4	965.5	
779.2	789.4	773.6	776.4	788.5	δ(Si–O–Si)
—	680.7	680.7	680.9	681.3	
			681.0	680.9	SiO stretching vibrations
—	—	—	667.8	668.5	
			622.3	619.3	[SiO ₄]
—	—	—	592.3	610.2	
			584.1	566.6	SiO deformation vibrations
—	—	—	547.7	516.2	
			501.8	502.0	
450.2	445.5	445.4	472.9	472.9	[CaO ₆]
			458.3	457.8	

stage varies from 12 to 20 days for the series of solutions with 20% P₂O₅, 7 to 10 days for 30% P₂O₅, and 5 to 7 days for 40% P₂O₅. For the duration of the second stage the change of the FFS viscosity of three-component oxide systems is small — $(0.9 - 1.5) \times 10^{-3}$ Pa · sec, which fully meets the technological requirements, so that the second stage can be determined as the interval of working viscosity for obtaining films.

The third stage corresponds to a transition of the system from a free-disperse into a bound-disperse system — from the “sol” state into a “gel” state. In this state solutions lose their film-forming power and remain suitable for obtaining disperse products.

Two waves are noted in plots of the viscosity versus time. This illustrates the characteristic cyclicity of the TEOS polycondensation processes depending on the accumulation of silanol groups or elemental oxygen radicals with OH end groups in the system. The latter form with ring closure of siloxanes and emergence of OH groups onto the external “surface” of ring formations as well as with physical-chemical

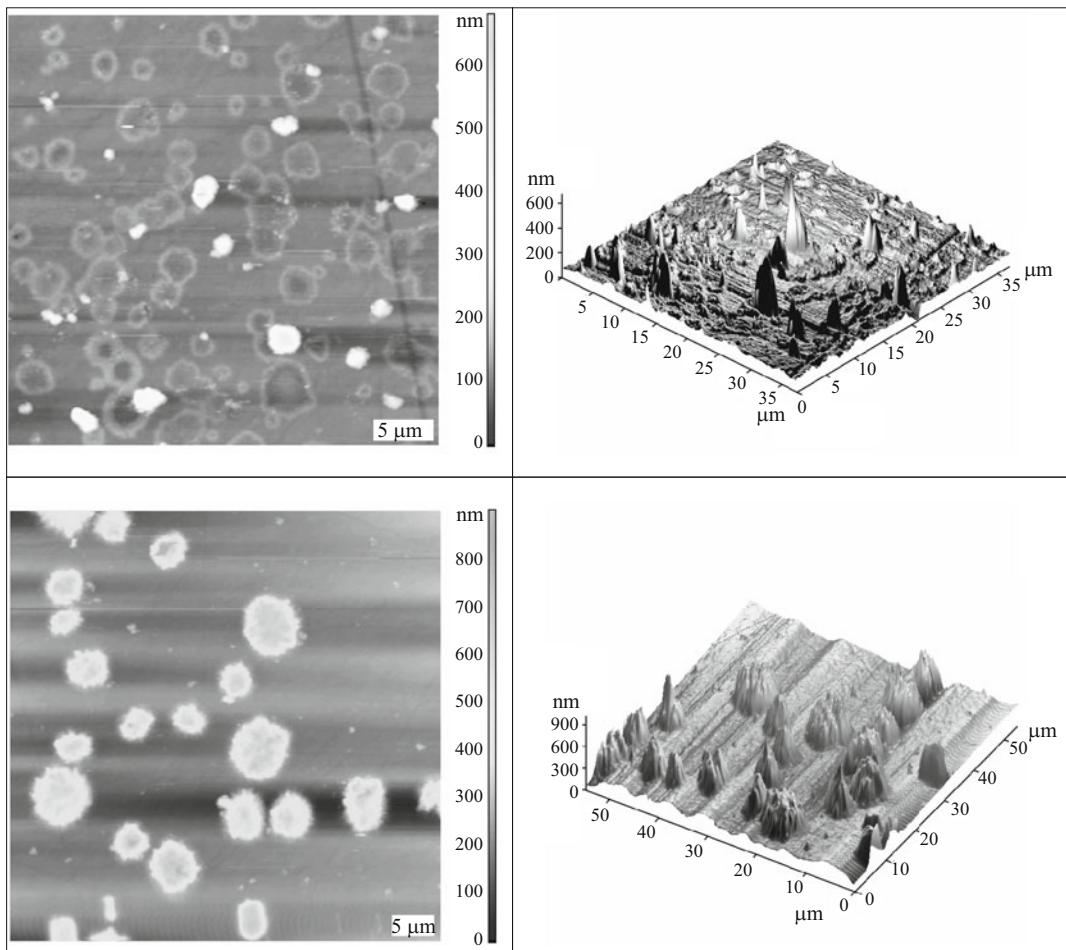


Fig. 5. Fragments of the surface of film with composition No. 43, according to atomic-force microscopy data.

transformations with formation of water and subsequent hydrolysis.

To study the physical-chemical processes occurring with the formation of oxide systems under the action of temperature, IR-spectroscopic analysis was performed on films deposited on the surface of a silicon substrate. Atomic-force spectroscopy was used to study their structure. The IR spectra of films corresponding to composition No. 43 are presented in Fig. 4: 50% SiO₂, 20% P₂O₅, and 30% CaO; the characteristics of the bands in the spectra of the films formed at 25°C and heat-treated at 60, 150, 500, and 800°C are presented in Table 1.

The IR-spectroscopy data show that adsorbed water and an organic solvent, characterized by the stretching vibrations of P=O, PO₄³⁻ groups, siloxane chains δ (Si—O—Si), and calcium bonds with oxygen, are present in the films formed at 25°C.

The presence of characteristic bands at 1166 and 1259 cm⁻¹ proves that water is present in the films right up to 800°C and that heat-treatment to 500°C completely removes organic compounds. The structure of the films is formed by the silicon-oxygen and phosphorus-oxygen

atomic groups, as attested by the presence of the bands 667 – 680, 590 – 620, 930 – 965 and 920 – 950, and 1040 – 1078 cm⁻¹ as well as the bands characterizing the vibrations of the tetrahedral groups SiO₄ (592 – 681 cm⁻¹) and PO₄ (929 – 1078 cm⁻¹). The group of bands in the range 550 – 750 cm⁻¹ can be attributed to symmetric vibrations of the bridge bonds Si—O—Si in the silicon-oxygen tetrahedra [6]. The absorption bands in the low-frequency region 400 – 550 cm⁻¹ are due to deformation vibrations of the O—Si—O bonds and stretching vibrations of the calcium-oxygen bonds in [CaO₆] octahedra.

The character of their IR spectra illustrates the process of systematic structuring of the films as a result of treatment at temperatures from 150 to 800°C. Differential-thermal analysis shows that crystallization processes are recorded in dry xerogel powder with heat-treatment to 700°C.

Atomic-force microscopy shows that for high SiO₂ content a uniform film coating is formed. Structured films form when the silicon oxide content is lowered to 50% or less. Images obtained by atomic-force microscopy of the surface of a film with composition No. 43 (50% SiO₂) are displayed in Fig. 5. The surface is distinguished by diverse relief,

which is formed above the base layer of the film by three types of elements. Craters giving rise to uniform porosity of the surface and forming as a result of gas emission are most numerous. The diameter of the craters varies over the range 1–5 μm. In all probability, the formation and subsequent growth of crystallites, which gives rise to structuring of a film, starts along their perimeter at the interface between phases. The presence of pores and cavities inside aggregates of crystallites, whose transverse size does not exceed 10 μm, supports this conclusion.

Sections with average transverse dimensions from 30 × 30 to 40 × 80 μm, on which two types of crystallites are located — pyramids, rarely forming extended rows, and sheaf-shaped aggregates — are discerned on the surface. The height of the relief elements — craters, single crystallites, and their aggregates — above the base layer of the film ranges from 20 to 300 nm on average, and the height of single aggregates reaches 600, 900 nm. The average thickness of the film does not exceed 90 nm.

CONCLUSIONS

Thin structured films and disperse products in the systems SiO₂–P₂O₅–CaO–(Na₂O) with content (wt.%) 10–85 SiO₂, 5–40 P₂O₅, 10–50 CaO, and 10 Na₂O were obtained by the sol-gel method from film-forming solutions of tetra-ethyl-ortho-silicate and phosphoric acid with addition of calcium and sodium salts.

The physical-chemical processes occurring in the solutions during aging and giving rise to a transition of the true solutions into colloidal solutions systematically through the “sol” into a “gel” state were studied. The solution viscosity is the criterion for the film-forming power. The critical value of the viscosity for obtaining high-quality films was determined

to be 5×10^{-3} Pa · sec, and the temporal range of the technological (working) viscosity for each composition, where structured films can be obtained from solutions by centrifuging and drawing, was established. It was shown that oxide systems form in the films and dispersions at temperatures to 600°C. The structure of the films is formed by silicon-oxygen and phosphorus-oxygen atomic groups in which [CaO₆] octahedra are also present. The films, obtained on silicon substrates, with the experimental compositions have average thickness up to 90 nm and high porosity. The surface of the films is characterized by an extended relief, so that the surface can be expected to have high adhesion properties.

REFERENCES

1. M. M. Sychev, “Prospects for using the sol-gel method in inorganic materials technology,” *Zh. Prikl. Khim.*, **63**(3), 489–498 (1990).
2. H. S. Nalwa and Stevenson Ranch (eds.), *Handbook of Nanostructured Biomaterials and Their Applications in Nanobiotechnology*, American Scientific Publishers, N.Y. (2005).
3. T. S. Petrovskaya, V. V. Kozik, and L. P. Borilo, “Thin-film formation in the silicophosphate system,” *Izv. Tomsk. Politekh. Univ. Ser. Khim.*, **316**(3), 23–27 (2010).
4. T. S. Petrovskaya, L. P. Borilo, V. V. Kozik, and V. I. Vereshchagin, “Structure and properties of nanoproducts of the system P₂O₅–SiO₂,” *Steklo Keram.*, No. 11, 29–33 (2008); T. S. Petrovskaya, L. P. Borilo, V. V. Kozik, and V. I. Vereshchagin, “Structure and properties of nanoproducts of the system P₂O₅–SiO₂,” *Glass Ceram.*, **65**(11–12), 410–414 (2008).
5. B. I. Beletskii and N. V. Svetskaya, “Silicon in living organisms and new-generation biocomposite materials,” *Steklo Keram.*, No. 3, 26–30 (2009); B. I. Beletskii and N. V. Svetskaya, “Silicon in living organisms and new-generation biocomposite materials (review),” *Glass Ceram.*, **66**(3–4), 104–108 (2009).
6. K. Nakanisi, *Infrared Spectra and Structure of Organic Molecules* [Russian translation], Mir, Moscow (1965).